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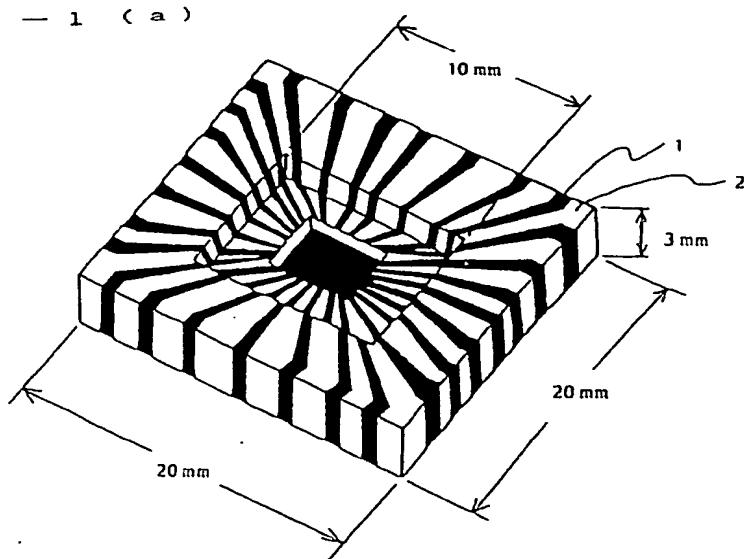
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(54) Two-color molded article for use in circuit formation.

(57) A two-color molded article, for use in the formation of electronic circuits, is produced by a two-color injection molding process comprising integrally molding a secondary side thermoplastic resin containing an inorganic filler with a molded article of a primary side thermoplastic resin comprising an easily platable resin composition having excellent adhesion between the molded article of the primary side thermoplastic resin and that of the secondary side thermoplastic resin, characterized in that the secondary side thermoplastic resin is a liquid crystal polyester resin composition containing a liquid crystal polyester of a weight-average molecular weight of 10000 or below as a base resin and having a melt viscosity (at a temperature of 310 °C and a shear rate of 1200 sec⁻¹) of 200 P or below

Fig — 1 (a)



TWO-COLOR MOLDED ARTICLE FOR USE IN CIRCUIT FORMATION

This invention relates to a molded article, for use in the formation of electronic circuits, produced by using thermoplastic resin compositions as injection molding materials and molding these resins by two-color injection molding.

The molded article of the invention is formed by two-color injection molding procedure in which a primary side thermoplastic resin is first molded to form a primary molded article of predetermined shape, subjecting the primary molded article to etching and catalyst application as a pretreatment for plating, setting the pretreated article in a second mold having a cavity which is in conformity with the entire shape of a molded article for use in circuit formation, filling with a secondary side thermoplastic resin the space in the second mold cavity unfilled by the primary molded article so as to leave the circuit-formation part of the primary molded article uncovered and integrally molding them by secondary molding. The molded article thus formed is subjected to electroless plating to form a circuit on the uncovered area of the primary side molded article having a circuit formed therein. When the primary side thermoplastic resin contains a plating catalyst, the final product can be obtained by subjecting to the pretreatments and electroless plating a molded article obtained by integrating the molded primary side thermoplastic resin with the molded secondary side thermoplastic resin. However, the adhesion in the molded article between the primary molded article and the secondary side resin is usually so poor that plating solution penetrates through the interface between the primary and secondary side molded resins during the step of electroless plating of the primary side molded article after the two-color molding. This penetration of plating solution causes such problems as corrosion of the formed circuit or peeling at the interface between the primary and secondary sides when the final product is used under severe conditions. These problems have been solved either by improving the adhesion at the interface, for example by improving the resin flow by elevating the cylinder temperature or the injection pressure of a molding machine during the secondary molding, or by reducing differences in the molding shrinkage between the primary side and the secondary side resins, for example by preheating the molded primary side resin to a temperature near the molding temperature of the secondary side resin, setting it in the cavity and performing the secondary molding.

However, these solutions have created further problems such as decreased mechanical strength due to the degradation of the resin, breakage of the primary side molded resin to the elevated injection pressure in the secondary molding and the deformation of the molded primary side resin due to the preheating. Even in those instances in which good adhesion has been achieved between the primary side resin and the secondary side resin and no problem has arisen of maintaining air tightness just after being molded, there has arisen a further problem of delamination due to heat hysteresis during a high-temperature/low-temperature cycle.

With a view to solving the abovementioned problems, the inventors of this invention have investigated means of improving the interfacial adhesion between the molded primary side resin and the molded secondary side resin in a molded article formed by packing and integrally molding the secondary side thermoplastic resin with the molded article of the primary side thermoplastics resin by two-color injection molding. The investigations led to the present invention, wherein a specified liquid crystal polyester resin composition of a very low melt viscosity, namely a melt processable polyester resin composition forming an anisotropic molten phase, has been found to be a very suitable raw material for the secondary side thermoplastic resin. This raw material can give a molded article for use in circuit formation, having improved adhesion between the primary side and the secondary side molded resins, and by further adding a silicone rubber and/or a thermoplastic elastomer to the material the molded article can keep high adhesion even when it is subjected to a load of a high temperature - low temperature heat shock cycle.

Namely, this invention provides a two-color molded article for use in circuit formation, formed by the two-color injection molding process comprising integrally molding a secondary side thermoplastic resin containing an inorganic filler with the molded article of a primary side thermoplastic resin comprising an easily platable resin composition and excellent in the adhesion between the molded article of the primary side thermoplastic resin and that of the secondary side thermoplastic resin, characterized in that a liquid crystal polyester resin composition containing a liquid crystal polyester of a weight-average molecular weight of 10000 or below as a base resin and having a melt viscosity (at a temperature of 310 °C and a shear rate of 1200 sec⁻¹) of 200 P or below is used as the secondary side thermoplastic resin.

The secondary side thermoplastic resin to be used in this invention is a liquid crystal polyester resin composition having a melt viscosity of 200 P or below when measured at a temperature of 310 °C and a shear rate of 1200 sec⁻¹, especially, a composition having a melt viscosity of 50 to 200 P. When the melt viscosity exceeds 200 P, imperfect molding is achieved as a result of short shot, etc., while when the melt

viscosity is below 50 P, resin flows out of the tip of the nozzle of an injection molding machine to cause problems such as unstable metering.

In order to obtain the liquid crystal polyester resin composition of such a low melt viscosity in this invention, it is necessary to control the kind (weight-average molecular weight) of the liquid crystal polyester resin, the amount of the inorganic filler added, etc. Namely, the liquid crystal polyester resin used should have a weight-average molecular weight of 1000 to 7000. If the liquid crystal resin has a weight-average molecular weight of 10000 or above, short shot occurs, so that the molding must be conducted by elevating the resin temperature or the injection pressure, which sometimes leads to the degradation of the resin and the breakage of the primary side molded article due to the elevated injection pressure. The molecular weight can be determined by gel permeation chromatography and other standard methods which do not involve the formation of polymer solutions, such as the determination of end groups by infra red spectroscopy of a compression-molded film. It is also possible to determine the molecular weight by applying the light scattering method to a solution of a polymer in pentafluorophenol.

The liquid crystal polyester resin material of the secondary side resin to be used in this invention contains an inorganic filler in such an amount as to retain the difficult platability of the resin and to give a melt viscosity of 200 P or below when measured under conditions of a temperature of 310 °C and a shear rate of 1200 sec⁻¹. The inorganic filler is not particularly limited and any fibrous, powdery or particulate or platy inorganic substances may be used according to the required duty.

Examples of the fibrous inorganic substance include inorganic fibrous substances such as glass fiber, carbon fiber, asbestos fiber, silica fiber, silica/alumina fiber, alumina fiber, zirconia fiber, boron fiber and potassium titanate fiber.

Examples of the powdery or particulate inorganic substance include carbon black, graphite, silica, quartz powder, glass beads, glass balloons, glass powder, metal oxides such as iron oxide, ferrite, silicon carbide, silicon nitride and boron nitride.

Examples of the platy inorganic substance include mica and glass flakes.

These inorganic fillers may be used alone or in the form of a mixture of at least two of them.

Fillers which are particularly desirably used are fibrous inorganic substances and ground products thereof, and examples thereof include glass fiber and milled glass fiber. The amount of the inorganic filler is 80 % by weight or below, desirably, 30 to 50 % by weight. From the viewpoints of the balance between platability and mechanical properties, milled glass fiber which is in between glass fiber and finely powdered glass is particularly desirable.

In using these inorganic fillers, it is desirable to use, if necessary, a binder or a surface treatment.

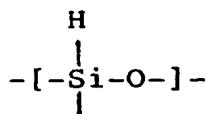
This liquid crystal polyester is a high-strength material having a self-reinforcing effect ascribable to its special molecular ordering and has a small dimensional distortion because of its low coefficient of linear expansion and low molding shrinkage. Further, it has a heat resistance of 220 to 240 °C in spite of its low melt viscosity and good flow. Further, it is highly chemically stable, is inert to other materials and is desirable as the secondary side thermoplastic resin. Thus, the liquid crystal polyester has excellent properties as the secondary side thermoplastic resin and its adhesive properties can be further improved by adding a silicone rubber and/or a thermoplastic elastomer thereto.

The polyorganosiloxane constituting the silicone rubber to be used in this invention may be one derived by replacing part of the methyl side chains and/or at least part of the chain terminals of, for example, dimethylpolysiloxane by at least one substituent (other than the above reactive functional groups) such as alkyl, aryl, haloalkyl, haloaryl, amino-modified alkyl, mercapto-modified alkyl, epoxy-modified alkyl, carboxyl-modified alkyl or polyether-modified groups, alcohol-modified groups, ester-modified groups or the like.

The silicone rubbers to be used in this invention are desirably powdery or particulate, and examples thereof include a millable silicone rubber formed by kneading an organopolysiloxane of a high degree of polymerization with an inorganic filler and a curing agent and crosslinking the mixture by heat vulcanization and a silicone rubber formed by crosslinking at least one organopolysiloxane having reactive groups by heating, ultraviolet radiation or the like in the presence of a catalyst.

Especially, a powdery or particulate addition type silicone rubber which can be crosslinked by the hydrosilylation addition reaction of an unsaturated group such as a vinyl group with

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in the presence of a platinum compound catalyst is desirable. As said powdery or particulate silicone rubber, one having a mean particle diameter of 0.1 to 100 μm is desirable, and one having a mean particle diameter of 1 to 20 μm is particularly desirable.

Although the thermoplastic elastomer to be used in this invention is not particularly limited as far as it has heat resistance and good dispersibility in the secondary side resin and good compatibility with it, desirable examples thereof include ethylene/ethyl acrylate copolymers, maleic anhydride-grafted ethylene/ethyl acrylate copolymers, nylon 4,6 and polyamide resin elastomers. When other elastomers are used, it sometimes happens that the elastomers themselves are decomposed because they have poor heat resistance and the melting temperature of the secondary side thermoplastic resin is high. Further, when an elastomer has poor compatibility though it has good heat resistance, it is not effective in improving the adhesion because of its poor state of dispersion.

The amount of the silicone rubber or the thermoplastic elastomer in this invention is 0.1 to 10 % by weight based on the total weight of the secondary side thermoplastic resin composition. More particularly, it is desirably 1 to 5 % by weight. When the silicone rubber and the thermoplastic elastomer are to be used together, it is desirable that the amount thereof should not exceed 15 % by weight based on the total weight of the composition.

Because the silicone rubber and the thermoplastic elastomer are added to the secondary side thermoplastic resin of this invention not for the purpose of reacting them with the liquid secondary side thermoplastic polyester, chemically inert ones are desirable. When these silicone rubber and thermoplastic elastomer are added to the liquid crystal polyester, the obtained composition is desired to take the so-called sea-island structure.

Further, the secondary side composition of this invention may contain other thermoplastic resins as auxiliaries within the range not detrimental to the intended object of this invention within the scope of this invention.

The thermoplastic resins to be used in this case are not particularly limited and examples thereof include polyolefins such as polyethylene and polypropylene, polyacetals (homo- and co-polymers), polystyrene, polyvinyl chloride, polyacrylate and copolymer thereof, polycarbonate, ABS, polyphenylene oxide, polyphenylene sulphide and fluororesin. These thermoplastic resins may be used also in the form of a mixture of at least two of them.

According to the required duty, it is also appropriate to add optionally well-known additives for ordinary thermoplastic and thermosetting resins, namely, plasticizers, stabilizers such as antioxidants and ultraviolet absorbers, antistatic agents, surface treatments, surfactants, flame retardants, colorants such as dyes and pigments, parting agents and lubricating agents for improving flow and mold release characteristics, and crystallization accelerators (nucleators).

The primary side thermoplastic resin to be used in this invention is an easily platable thermo-plastic resin, and is not particularly limited as far as it is a thermoplastic resin which can be bonded to metal by plating and can be surface-treated to have an adhesion to a plating metal above a certain level. It may be suitably selected according to the condition of use of the molded article. Because it is necessary for the purpose of use that the molded article for use in circuit formation meet requirements such as solderability, durability and mechanical properties, it is desirable that the molded primary side resin is a material which is heat-resistant, has mechanical strengths, good dimensional stability and a coefficient of linear expansion very close to that of a metal, and does not cause facile peeling of the plating metal.

Examples of the primary side thermoplastic resin suitable in this invention from this viewpoint include liquid crystal polyesters (melt-processable polyesters which can exhibit anisotropy when melted), polysulphones, polyether sulphones, polyether imides, polyphenylene sulphides and polyether ketones.

Especially, the liquid crystal polyesters can form a fine wire circuit because of good moldability and are thermoplastic resins with excellent properties such as rigidity, heat distortion resistance and dimensional stability. Further they are materials which are most suitable for the primary side molded article of this invention in respect that a liquid crystal polyester resin composition is used as the secondary side thermoplastic resin in this invention.

A liquid crystal polyester suitably used in this invention generally has a weight-average molecular weight of about 2000 to 200000, desirably, about 10000 to 50000, particularly desirably, about 20000 to 25000. On the other hand, a suitable aromatic polyester amide generally has a molecular weight of about 5000 to 50000, desirably, about 10000 to 30000, for example, 15000 to 17000.

The abovementioned aromatic polyester and polyester amide generally have an inherent viscosity (I.V.) of at least about 2.0 dl/g, for example, about 2.0 to 10.0 dl/g when dissolved in pentafluorophenol at 60 °C in a concentration of 0.1 % by weight.

A liquid crystal polyester in general is platable with difficulty, but it is easily made platable so as to be

used as the primary side thermoplastic resin by adding to the resin at least one inorganic filler selected from the group consisting of the Group II elements of the periodic table and oxides, sulphates, phosphates, silicates and carbonates thereof, aluminium, silica, tin, antimony, bismuth and oxides thereof, and palladium chloride.

5 Examples of the inorganic filler include oxides such as magnesium oxide, calcium oxide, barium oxide and zinc oxide; magnesium phosphate; calcium phosphate; barium phosphate; zinc phosphate; magnesium pyrophosphate; calcium pyrophosphate; sulphates such as barium sulphate; silicates such as magnesium silicate, calcium silicate, aluminium silicate, kaolin, talc, clay, diatomaceous earth and wollastonite; magnesium carbonate; calcium carbonate; barium carbonate; and zinc carbonate.

10 It is also possible to add the above mentioned fibrous, powdery or particulate or platy inorganic filler together with the above inorganic filler to the primary side thermoplastic resin. A metallic fiber or foil can also be used. It is also possible to use other thermoplastic resins, additives, etc., used in the secondary side resin.

15 The liquid crystal polyesters desirably used as both of the primary side and the secondary side thermoplastic resins in this invention are melt-processable polyesters which can assume a molten state in which the polymer molecular chains are regularly ordered in parallel. A state in which molecules are so ordered is sometimes referred to as a liquid crystal state or a nematic phase of a liquid crystal substance. The molecule of such a polymer is generally long and flat, has a considerably high rigidity along the major molecular axis and is usually composed of a plurality of chain extending bonds lying in a coaxial or parallel 20 relation.

25 The nature of an anisotropic molten phase can be confirmed by the conventional polarization test performed by using crossed polarizers. More particularly, an anisotropic molten phase can be confirmed by using a Leitz polarization microscope and observing a molten sample mounted on a Leitz hot stage in a nitrogen atmosphere at a magnification of 30 X. Even when the polymer of this invention is in a static molten state when observed between crossed polarizers, it can transmit a polarized light and exhibits 30 optical anisotropy.

The liquid crystal polymer suitable for use in this invention has a tendency toward being substantially insoluble in an ordinary solvent, so that it is unsuitable for solution processing. However, these polymers, as already mentioned, can be easily processed by usual melt processing techniques.

35 The polymer showing an anisotropic molten phase, used in this invention, is desirably an aromatic polyester or an aromatic polyester amide, and a polyester partially comprising both of an aromatic polyester and an aromatic polyester amide in the same molecule is a desirable example. A particularly desirable example is a liquid crystal aromatic polyester or aromatic polyester amide containing at least one compound selected from the group consisting of an aromatic hydroxy carboxylic acid, an aromatic hydroxy amine and an aromatic diamine as the constituent.

More particularly, examples thereof include

1) a polyester mainly consisting of at least one member selected from an aromatic hydroxy carboxylic acid and derivatives thereof,

2) a polyester mainly consisting of

40 (a) at least one member selected from an aromatic hydroxy carboxylic acid and derivatives thereof,

(b) at least one member selected from among an aromatic hydroxy carboxylic acid, an alicyclic dicarboxylic acid and derivatives thereof, and

(c) at least one member selected from among an aromatic diol, an alicyclic diol, an aliphatic diol and derivatives thereof,

45 3) a polyester amide mainly consisting of

(a) at least one member selected from an aromatic hydroxy carboxylic acid and derivatives thereof,

(b) at least one member selected from among an aromatic hydroxy amine, an aromatic diamine and derivatives thereof, and

(c) at least one member selected from among an aromatic dicarboxylic acid, an alicyclic dicarboxylic acid and derivatives thereof, and

50 4) a polyester amide mainly consisting of

(a) at least one member selected from an aromatic hydroxycarboxylic acid and derivatives thereof,

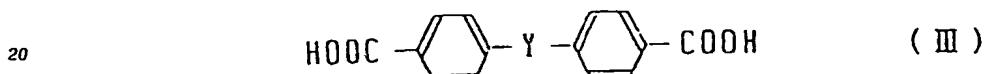
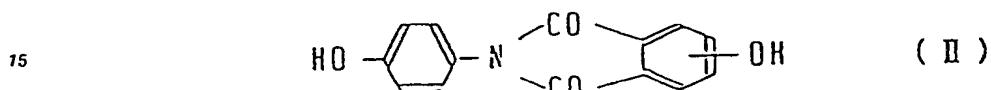
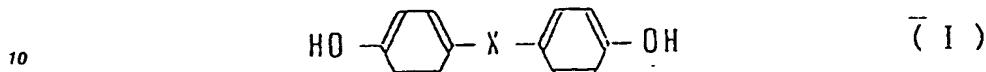
(b) at least one member selected from among an aromatic hydroxy amine, an aromatic diamine and derivatives thereof,

(c) at least one member selected from among an aromatic dicarboxylic acid, an alicyclic dicarboxylic acid and derivatives thereof, and

(d) at least one member selected from among an aromatic diol, an alicyclic diol, an aliphatic diol and derivatives thereof.

If necessary, a molecular weight modifier may be used together with the above constituents.

Desirable examples of particular compounds which constitute the liquid crystal polyester of this invention include naphthalene compounds such as 2,6-naphthalene-dicarboxylic acid, 2,6-dihydroxynaphthalene, 1,4-dihydroxynaphthalene, and 6-hydroxy-2-naphthoic acid; biphenyl compounds such as 4,4'-diphenyldicarboxylic acid and 4,4'-dihydroxybiphenyl; compounds represented by the following general formulae (I), (II) and (III):



wherein X is a group selected from among an alkylene (C₁-C₄), an alkylidene, -O-, -SO-, -SO₂-, -S- and -CO-, and

25 Y is a group selected from -(CH₂)_n-n- (wherein n is 1 to 4) and -O(CH₂)_nO- (wherein n is 1 to 4), p-substituted benzene compounds such as p-hydroxybenzoic acid, terephthalic acid, hydroquinone, p-aminophenol and p-phenylenediamine and ring-substituted derivatives thereof (wherein the substituent is selected from among chloro, bromo, methyl, phenyl and 1-phenylethyl); and m-substituted benzene compounds such as isophthalic acid and resorcinol.

30 The liquid crystal polyester used in this invention may contain, in addition to the abovementioned constituents, a polyalkylene terephthalate which does not exhibit any anisotropic molten phase as part of the same molecular chain. The number of carbon atoms of the alkyl group in this case is 2 to 4.

Preferred examples of the liquid crystal polyester are those containing, among the abovementioned constituents, at least one compound selected from among a naphthalene compound, a biphenyl compound 35 and a p-substituted benzene compound as the essential component. Particularly desirable examples among the p-substituted benzene compounds are p-hydroxybenzoic acid, methylhydroquinone and 1-phenylethylhydroquinone.

Examples of the compounds having esterifiable functional groups as constituents and the desirable polyesters forming an anisotropic molten phase to be used in this invention are described in Japanese 40 Patent Publication No 36633/1988.

This invention relates to a two-color molded article for use in circuit formation, which is formed by molding the secondary side thermoplastic resin with the molded primary side thermoplastic resin constituted as abovementioned and wherein the liquid crystal polyester of the secondary side thermoplastic resin containing an inorganic filler such as glass fiber, milled glass fiber or an inorganic powder has 45 decreased anisotropy and gives a molded article having a very low coefficient of linear expansion which is the same in all directions irrespective of the resin flow during molding and having heat resistance and heat shock resistance.

When a silicone rubber and/or a thermoplastic elastomer are added to the liquid crystal polyester, the molded article of this invention has a decreased post shrinkage and an improved adhesion between the 50 primary side and secondary side resins, and retains the reliability of a product for a long time.

Examples

55 This invention will now be described in more detail with reference to the following non-limiting Examples. Reference is made in the Examples to the accompanying drawings, in which:

Figure 1(a) is a perspective view of a two-color molded article prepared in the Examples,

Figure 1(b) is an enlarged view of the plated part (primary side thermoplastic resin) of said article, and

Figure 2 is a perspective view representing the state in which a lid is laid on said molded article.

The reference numerals in these figures indicate the following components:

- 1: primary side thermoplastic resin
- 2: secondary side thermoplastic resin
- 5 3: glass lid.

Examples 1 to 10 and Comparative Examples 1 and 2

10 Each of the following seven liquid polyester resins was mixed with an inorganic filler, etc. in a composition ratio as specified in Table 1 to form the primary side thermoplastic resin composition or the secondary side thermoplastic resin composition. The thus-obtained compositions were pelletized at 300 to 320 °C in a usual manner and these pellets were molded into the shapes shown in Figure 1 by two-color molding to evaluate the molded articles thus formed. The cylinder temperature of the injection molding machine used was set at 300 °C. Table 1 gives the results of measurement.

15 The liquid crystal polyesters used in the Examples were those having the following structural units:

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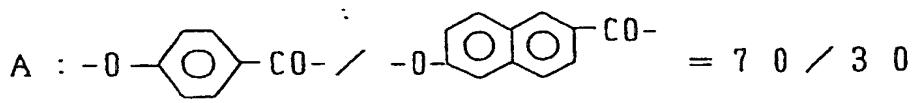
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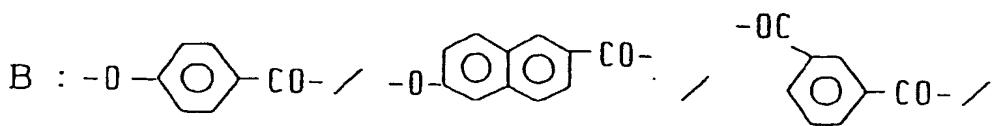
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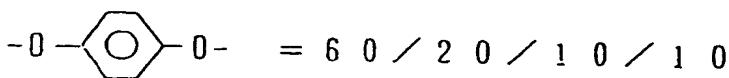
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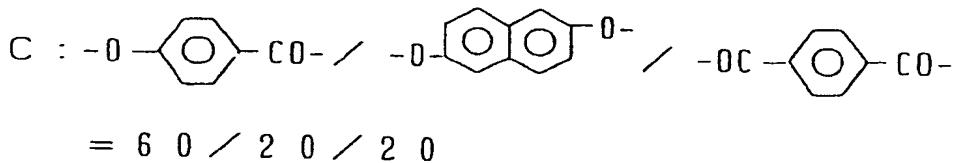
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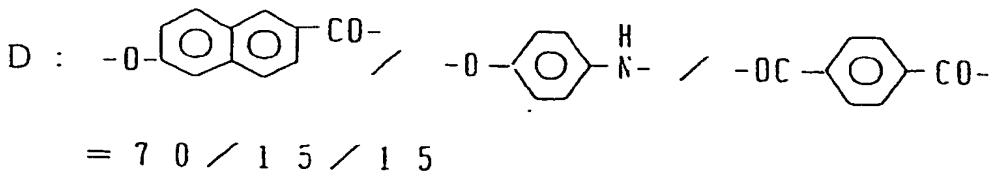
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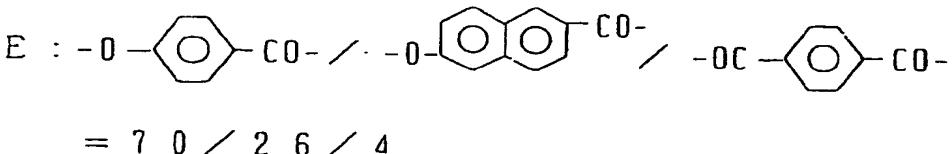
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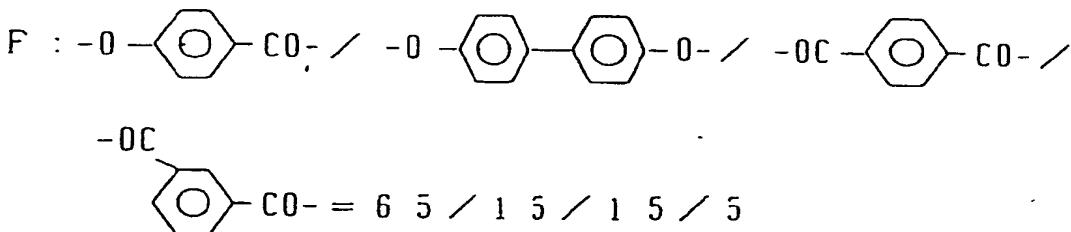
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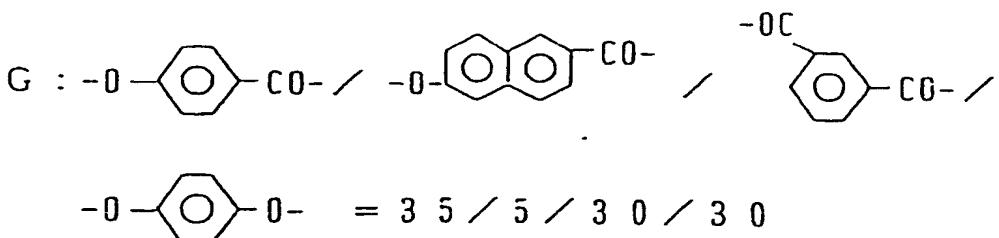
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(The above numbers represent molar ratios)

The silicone rubber A used here was a powdery or particulate (mean particle diameter of 8 μm) silicone rubber prepared by crosslinking a vinyldimethylpolysiloxane with a dimethylpolysiloxane having a



10 by addition reaction in the presence of a platinum compound catalyst. The silicone rubber B was one derived by replacing part of the methyl groups of the silicone rubber A by epoxy groups.

The methods for the measurement of the properties described in the following Examples and the evaluation methods were as follows:

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Measurement of Weight-Average Molecular Weight

A gel permeation chromatograph composed of a liquid feed pump, a sample injector, a high temperature thermostatic chamber, a separator column, a differential refractive index detector (DRI), a small-angle laser beam scattering photometer, a personal computer for processing control data, etc was used to feed about 150 μl of a 0.1 wt. % polymer solution prepared by dissolving pellets of a liquid crystal polyester resin composition in pentafluorophenol through the injector to the apparatus uniformly set at 60 °C, separating the polymer fractions through a polystyrene gel treatment by utilizing the difference in molecular weight, sending the separated fractions to DRI and processing the obtained data to determine the molecular weight.

Ink Penetration Test

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A molded article shown in Figure 1 was immersed in an ink solution (a methanolic solution of red ink) for 5 minutes to the depth of a half of the thickness of the article with the upside thereof being directed upward to observe the presence or absence of penetrated ink in the area of contact between the molded primary side resin and the molded secondary side resin at the recessed central part of the molded article under a microscope.

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Gross Leak Test

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As shown in Figure 2, the recess of a two-color molded article of Figure 1 was covered with a glass plate by using an epoxy adhesive and the covered article was immersed in an inert liquid (Fluoroinert F40, a product of 3M)(at 125 °C) to evaluate the adhesion between the primary side and secondary side molded articles in terms of the emergence or non-emergence of bubbles from the area of contact between the primary side and the secondary side resins and the time required for the first bubble to be recognized. The case where no bubble was recognized after immersion for 30 minutes was designated as "no".

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A sample prepared by drying the same sample by heating at 150 °C for 1 hour and immersing it in a soldering bath at 260 °C for 10 seconds was subjected to the similar gross leak test. The case where no bubble was recognized after immersion for 10 minutes was taken as a measure of adhesion, and this state was designated as "no".

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Examples 11 to 13

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Molded articles were prepared for evaluation in the same manner as that of Examples 1 to 10 except that polyphenylene sulphide (PPS) or polyethylene terephthalate (PET) was used instead of the liquid crystal polyesters of Examples 1 to 10 as the base resin to prepare primary side thermoplastic resin compositions listed in Table 2. Table 2 shows the results of measurement.

Examples 14 to 21

Molded articles of the compositions specified in Table 3 were prepared for evaluation in the same manner as that of Examples 1 to 10 by using liquid crystal polyesters B,C and D as the primary side thermoplastic resins and liquid crystal polyester A as the secondary side thermoplastic resin. Table 3 gives the results of measurement.

Comparative Example 3

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Preparation of molded articles was attempted in the same manner as that of Examples 14 to 16 except that liquid polyester A of a high weight-average molecular weight (MW : 25000) was used as the secondary side thermoplastic resin. However, the solution viscosity of the secondary resin composition was 691P, so that the molding of the secondary side resin was impossible.

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Table I

Properties	Secondary side composition							
	Primarily side composition	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7
liquid crystal polyester (wt%)(M=25000)	A 50	A 50	A 50	A 50	A 50	A 50	A 50	A 50
milled glass fiber (wt%)	15	15	15	15	15	15	15	15
calcium pyrophosphate (wt%)	35	35	35	35	35	35	35	35
liquid crystal polyester (wt%)(M=35000)	A 45	A 45	B 45	C 45	D 45	E 45	F 45	G 45
milled glass fiber (wt%)	50	50	50	50	50	50	50	50
silicone rubber A (wt%)	5	—	5	5	5	5	5	5
silicone rubber B (wt%)	—	5	—	—	—	—	—	—
melt viscosity of resin(P) composition	100	120	108	121	112	123	109	118
moldability	yes	yes	yes	yes	yes	yes	yes	yes
ink penetration test	no	no	no	no	no	no	no	no
gross leak test (time required for the first bubble to be recognized: min)	no	no	no	no	no	no	no	no
gross leak test after immersion in soldering bath (time required for the first bubble to be recognized: min)	no	no	no	no	no	no	no	no

Table I (contd.)

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		Ex. 9	Ex. 10	Comp. 1 Ex.	Comp. 2 Ex.
Primary side composition	liquid crystal polyester (wt%) (MW=25000)	A 50	A 50	A 50	A 50
	milled glass fiber (wt%)	15	15	15	15
	calcium pyrophosphate (wt%)	35	35	35	35
Secondary side composition	liquid crystal polyester (wt%) (MW=3500)	A 50	B 50	A 100	B 100
	milled glass fiber (wt%)	50	50	—	—
	silicone rubber A (wt%)	—	—	—	—
	silicone rubber B (wt%)	—	—	—	—
Properties	melt viscosity of resin (P composition)	98	101	48	50
	moldability	yes	yes	yes	yes
	ink penetration test	no	no	yes	yes
	gross leak test (time necessary for the first bubble to be recognized: min)	20	20	≤ 1	≤ 1
	gross leak test after immersion in soldering bath (time necessary for the first bubble to be recognized: min)	≤ 10	≤ 10	≤ 1	≤ 1

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Table 2

			Ex. 11	Ex. 12	Ex. 13
5	Primary side composition	thermoplastic resin (wt%)	P P S 60	P P S 40	P E T 50
		milled glass fiber (wt%)	40	60	30
		calcium pyrophosphate (wt%)	—	—	20
10	Secondary side composition	liquid crystal polyester (MW=3500) (wt%)	A 50	A 45	A 45
		milled glass fiber (wt%)	50	50	50
		silicone rubber A (wt%)	—	—	5
		silicone rubber B (wt%)	—	—	—
15	Properties	melt viscosity of resin composition (P)	98	101	101
		moldability	yes	yes	yes
		ink penetration test	no	no	yes
		gross leak test (time required for the first bubble to be recognized: min)	20	no	no
20		gross leak test after immersion in soldering bath (time required for the first bubble to be recognized: min)	≤ 10	no	no
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Table 3

	Ex. 14	Ex. 15	Ex. 16	Ex. 17	Ex. 18	Ex. 19	Ex. 20	Ex. 21
Primary side composition	B	C	D	B	B	B	B	B
Secondary side composition	50	50	50	50	50	50	50	50
Properties								
moldability	yes	yes	yes	yes	yes	yes	yes	yes
ink penetration test	no	no	no	no	no	no	no	no
Gross leak test (time required for the first bubble to be recognized: min)	no	no	no	no	no	no	no	no
Gross leak test after immersion in soldering bath (time required for the first bubble to be recognized: min)	no	no	no	no	no	no	no	no
Properties								
melt viscosity of resin composition	(P)	52	52	54	78	80	50	53
secondary side composition	liquid crystal polyester (Mn=25000) milled glass fiber calcium pyrophosphate	(wt%) 15 35	(wt%) 15 35	(wt%) 65	(wt%) 65	(wt%) 65	(wt%) 65	(wt%) 65
Properties								
silicone rubber A	(Mn=7000)	30	30	30	30	30	30	30
silicone rubber B	(Mn=5000)	5	5	5	—	—	—	—
maleic anhydride-grafted ethylene/ acyl acrylate	(Mn=5000)	—	—	5	—	—	—	—
acrylic acid/ethyl acrylate	(Mn=5000)	—	—	—	—	5	—	—
nylon 4,6	(Mn=5000)	—	—	—	—	—	5	—
polyamide elastomer	(Mn=5000)	—	—	—	—	—	—	5

65 Claims

1. A two-color molded article for use in circuit formation, formed by the two-color injection molding process comprising integrally molding a secondary side thermoplastic resin containing an inorganic filler with the

molded article of a primary side thermoplastic resin comprising an easily platable resin composition and excellent in the adhesion between the molded article of the primary side thermoplastic resin and that of the secondary side thermoplastic resin, characterized in that a liquid crystal polyester resin composition containing a liquid crystal polyester of a weight-average molecular weight of 10000 or below as a base resin and having a melt viscosity (at a temperature of 310 °C and a shear rate of 1200 sec⁻¹) of 200 P or below is used as the secondary side thermoplastic resin.

5. A two-color molded article according to claim 1, wherein the primary side thermoplastic resin is selected from liquid crystal polyesters, polysulphones, polyether sulphones, polyether imides, polyphenylene sulphides and polyether ketones.

10. 3 A two-color molded article according to claim 1 or claim 2, wherein the primary side thermoplastic resin contains an inorganic filler.

4. A two-color molded article according to any preceding claim, wherein the secondary side thermoplastic resin contains 0.1 to 10 wt% (based on the whole composition) of a silicone rubber and/or a thermoplastic elastomer.

15. 5. A two-color molded article according to claim 4, wherein the secondary side thermoplastic resin contains a powdery or particulate silicone rubber.

6. A two-color molded article according to claim 5, wherein the secondary side thermoplastic resin contains silicone rubber having a mean particle diameter of 0.1 to 100 µm.

7. A two-color molded article according to claim 4, wherein the secondary side thermoplastic resin contains a thermoplastic elastomer selected from ethylene/ethyl acrylate copolymer resins, maleic anhydride-grafted ethylene/ethyl acrylate copolymer resins, nylon 4,6 and polyamide resin elastomers.

20. 8. A two-color molded article according to any preceding claim, wherein the molded article of the primary side is one pretreated for plating.

9. A two-color molded article according to any preceding claim, wherein the liquid crystal polyester is selected from an aromatic polyester, an aromatic polyester amide and a polyester partially comprising both of an aromatic polyester and an aromatic polyester amide in the same molecule.

25. 10. A two-color molded article according to claim 9, wherein the liquid crystal polyester is a liquid crystal aromatic polyester or aromatic polyester amide containing at least one compound selected from the group consisting of an aromatic hydroxy carboxylic acid, an aromatic hydroxy amine and an aromatic diamine.

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Fig — 1 (a)

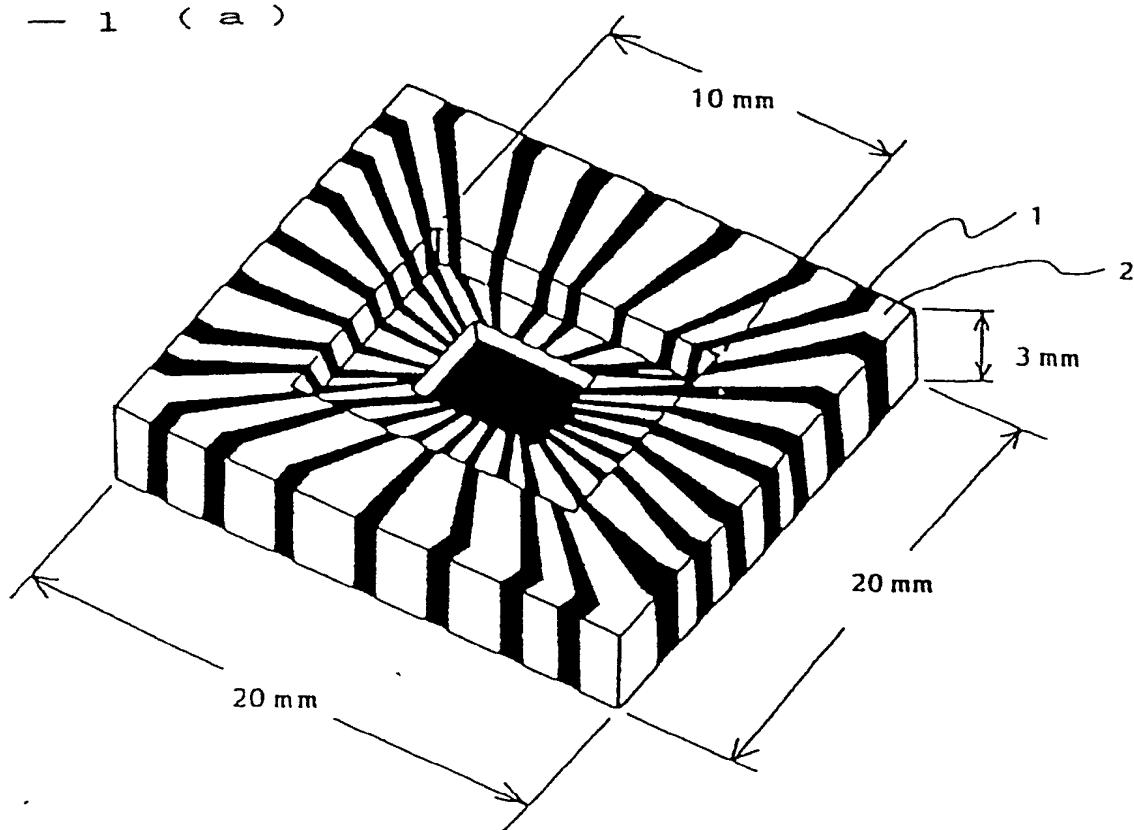


Fig — 1 (b)

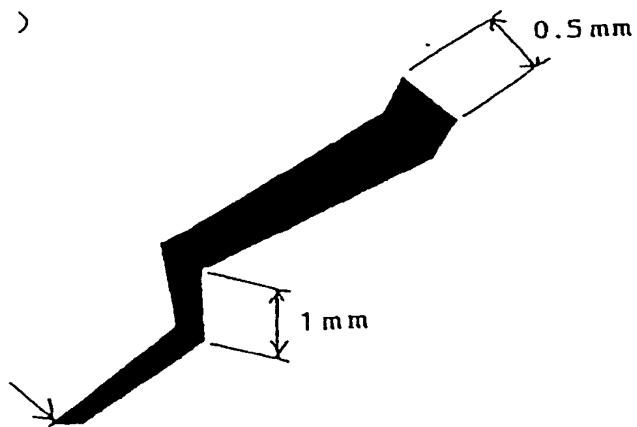
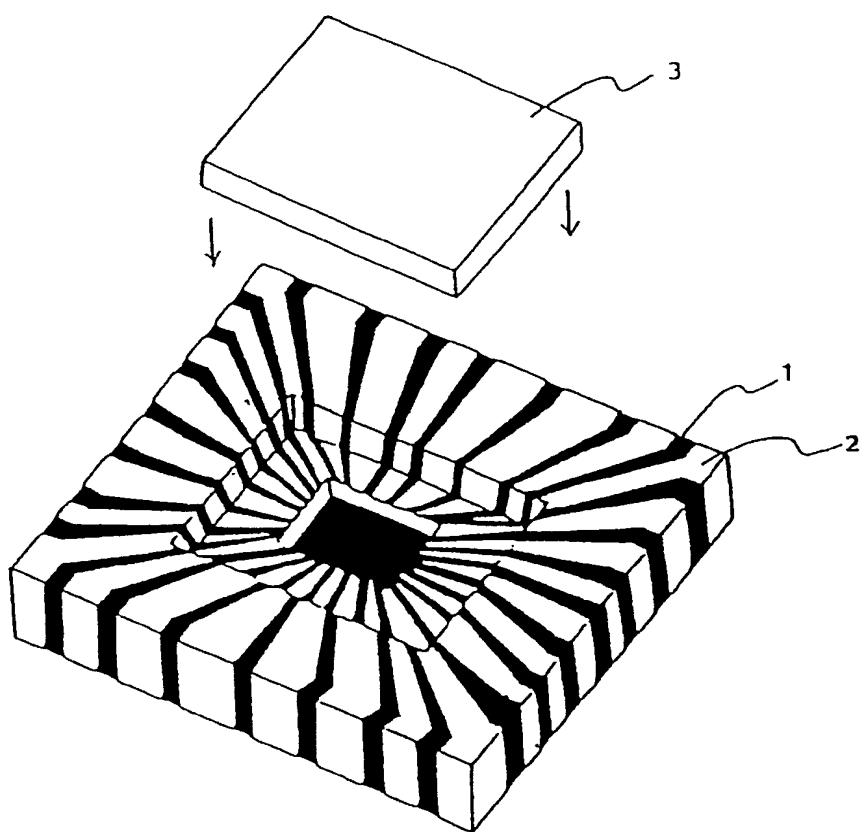


Fig — 2





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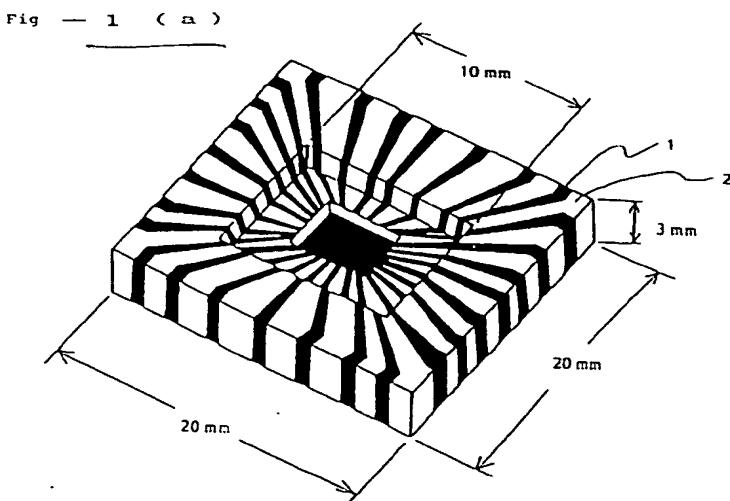
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⑳ Two-color molded article for use in circuit formation.

㉑ A two-color molded article, for use in the formation of electronic circuits, is produced by a two-color injection molding process comprising integrally molding a secondary side thermoplastic resin (2) containing an inorganic filler with a molded article of a primary side thermoplastic resin (1) comprising an easily platable resin composition having excellent adhesion between the molded article of the primary

side thermoplastic resin and that of the secondary side thermoplastic resin, characterized in that the secondary side thermoplastic resin is a liquid crystal polyester resin composition containing a liquid crystal polyester of a weight-average molecular weight of 10000 or below as a base resin and having a melt viscosity (at a temperature of 310 °C and a shear rate of 1200 sec⁻¹) of 200 P or below





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REPORT

Application Number

EP 90 31 1724

DOCUMENTS CONSIDERED TO BE RELEVANT					
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)		
A	WORLD PATENTS INDEX LATEST Section Ch, Week 8731, Derwent Publications Ltd., London, GB; Class A, AN 87-21630 & JP-A-62 141 064 (POLYPLASTICS) 24 June 1987 * abstract ** - - -	1,2,9	H 01 L 23/14		
A	WORLD PATENTS INDEX LATEST Section Ch, Week 8911, Derwent Publications Ltd., London, GB; Class A, AN 89-08006 & JP-A-1 030 722 (MEIKI) 1 February 1989 * abstract ** - - -	1			
A	EP-A-0 165 705 (BRITISH TELECOM) * page 5, line 6 - line 18 *** page 8, line 15 - page 9, line 30 .. - - -	1,2,8			
A	EP-A-0 264 290 (POLYPLASTICS) * claim 1 ** - - - -	1-3,9,10			
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl.5)		
			H 01 L		
Place of search	Date of completion of search	Examiner			
The Hague	15 October 91	GREENE S.K.			
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